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LAWRENCE LIVERMORE LABORATORY
University of California/Livermore, California

MICROWAVE ROTATIONAL SPECTROSCOPY: A PHYSICAL

TECHNIQUE FOR SPECIFIC POLLUTANT MONITORING

Lawrence W. Hrubesh

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Lawrence W. Hrubesh
University of California, Lawrence Livermore Laboratory
Livermore, California 94550

I. Introduction

Of the physical techniques available for trace-gas pollutant detection, the direct interaction of electromagnetic radiation with molecules is potentially the most selective and specific. This is so because such interactions occur at fixed energies that are governed by laws of quantum physics. They can be observed in either emission or absorption as sharp resonances within the electromagnetic spectrum. Thus, they offer a distinct fingerprint of the kind of molecule causing resonance.

Different types of molecular motions have different energies and thus interact with limited ranges of electromagnetic radiation. For example, the electronic motion in molecules is highly energetic and interacts with ultraviolet and visible radiation (> 10,000 wavenumbers). Molecular vibrations are of lower energy and can affect infrared radiations (100 to 10,000 wavenumbers). At even lower energies, molecular rotations can interact with microwave radiation (1 to 100 wavenumbers). Absorption spectroscopy, particularly in the microwave region, is a promising technique for gaseous pollutant monitoring.

II. Properties of microwave rotational spectroscopy

Rotational resonance absorption spectra are very sensitive to small changes in molecular structure; they are distinctly different even for isotopic species of the same molecule. Since all molecules have significantly different structural configurations, their rotational spectra offer a means to distinguish each within a mixture. The resolution of rotational resonances is extremely high because they are characteristically very sharp at low pressures and microwave frequencies. At pressures lower than 0.1 Torr the linewidths can be less than 50 kHz, which corresponds to a resolution of nearly 1 ppm. Additionally, it is not difficult to obtain highly stable microwave radiation that can be tuned electronically to any frequency of interest in a time less than 1 s. The combination of definite spectral identity, high resolution, and accuracy of measurement make this technique uniquely capable of inherently high qualitative specificity. In fact, a recent study [1] has indicated that the stronger absorbing molecules can be identified in a mixture with greater than 95% certainty by measuring only a single microwave rotational absorption line.

A very important property of this technique is the quantitative content of its signals. It is known that the spectrometer response at the peak of a rotational resonance is directly related to the concentration of the gas responsible for the absorption [2]. Moreover, for certain experimental conditions this response is known to be linear from the minimum detectable limits to 100% concentrations [3,4]. Hence, a microwave rotational spectrometer can be calibrated to give the concentration of the absorbing species directly.

Many of the common pollutant gases have known microwave rotational spectra, and most have at least one line with an absorption coefficient (the fractional power absorbed by the sample per unit of absorption path length) as large as 10^{-5} cm^{-1}. It is presently possible to construct a microwave spectrometer capable of detecting an absorption with a coefficient as small as 10^{-12} cm^{-1}. This suggests that it is quite possible to detect fractional abundances as small as 100 ppb for many common pollutants and nearly 10 ppb for some selected gases that have more intense absorptions (NH_3, for example). Very little total sample is needed to detect an absorption. For the stronger absorbing gases, about 10^{-12} mol is sufficient.

Several limitations of microwave rotational spectroscopy should be noted. In order to have a rotational spectrum, a molecule must be polar. Generally, stronger rotational spectra are obtained for molecules having larger dipole moments. Most small molecules possess a permanent electric dipole moment, but a few — such as carbon dioxide, benzene, and mononuclear diatomics — have a truly symmetric charge distribution; these cannot be detected by microwave spectroscopy. More than 90% of the common gaseous pollutants of present interest, however, are polar, and the microwave rotational spectra of most of them have been observed and catalogued.

Microwave rotational spectroscopy is generally limited to the study of molecules having fewer than 20 atoms. Larger molecules than this usually have quite dense and immensely complicated spectra due to splitting caused by intermolecular interactions. Consequently, rotational spectra of large molecules are rarely catalogued. This is not a great limitation for pollutants, however, because most molecules of interest are of the small, more reactive variety

A more profound limitation of this technique for pollutant monitoring is the necessity of operating at low pressures. Operating sample pressures near 10^{-2} Torr are desirable to insure high specificity. Higher pressures induce collisional broadening of the resonant absorptions with a subsequent decrease in peak resolution. For normal broadening mechanisms, the linewidth of a rotational absorption line is proportional to the pressure over a wide range. Operating pressures greater than 10 Torr would reduce the resolution to an unacceptable level for monitoring purposes.

III. Instrumentation

A conventional microwave rotational spectrometer (see Fig. 1) has the essential elements of any spectrometer: a radiation source, an absorption cell containing the sample, and a detector. The radiation source is a voltage-tunable microwave generator (backward-wave or klystron oscillator) capable of delivering milliwatts of continuous radiation at any frequency within its operating range. The radiation is allowed to pass through at least a 1-m length of rectangular waveguide; the major length of the waveguide is vacuum sealed and used as the sample container. The detector generally used is a silicon crystal diode capable of rectifying the high microwave frequencies. A rotational absorption can actually be observed in such a system by noting the dip in the crystal diode output current (or voltage) as the microwave oscillator is swept in frequency through the range included by the resonant absorption of the molecule. Higher sensitivity, however, is derived from the use of the electric-field modulation applied through the gas sample (Stark effect), which has the effect of chopping the signal seen at the detector; ac amplification and phase-sensitive detection can then be used to substantially increase the signal-to-noise ratio. The obtainable sensitivity for such a system is directly proportional to the length of the sample cell. However, the attenuation of energy in the waveguide walls limits the length to some optimum value.

Another way to obtain a long absorption path length is with a microwave resonator. A resonator is defined as any configuration of reflective surfaces that can store electromagnetic energy for intervals longer than one period of oscillation of the microwave radiation. At resonance the microwave radiation makes multiple reflections between the walls of the cavity. If the gas sample fills that space, the effective absorption path length through the gas is the product of the wall separation and the number of reflections. A measure of the ability of a resonator to store energy is given by the quality factor, Q. Some resonators (particularly the Fabry-Perot type) can be constructed with a very high Q and have large effective-absorption path lengths for gas samples. Other advantages of the resonator are its compact size, its large volume-to-surface ratio, and the stability of its resonance frequency. Indeed, these are just the properties needed for a potentially portable microwave spectrometer system.

In the past few years, solid-state diodes that can generate microwave energy directly from dc have become available. The most popular of these, the Gunn-effect diode, can produce more than 20 mW of continuous microwave energy at frequencies up to 60 GHz from a 4-V, 1/2-A dc supply. Most important, however, is that the output frequency of such diodes can be controlled directly by the resonant frequency of a resonant cavity. This is possible

because of the inherent characteristics of a bulk negative-resistance element (Gunn diode) coupled directly to an energy storage device such as the resonator.

The combination of a dc-powered, solid-state source and a compact, high-Q cavity resonator is the basis for a very simple, but highly sensitive, microwave spectrometer system [5].

IV. A Gunn-diode microwave-cavity spectrometer

A Gunn-diode microwave cavity spectrometer designed to monitor specific microwave spectral lines is shown in block form in Fig. 2. A Gunn-effect diode capable of 5-mW output power at frequencies near the frequency of interest is mounted in a small section of waveguide. The waveguide is shorted on one end, and the other end is coupled to a high-Q, Fabry-Perot-type resonator through a small hole in the flat plate of the resonator. The other plate of the resonator has a spherical concave surface with an optimum radius of curvative to minimize dispersive losses and maximize the quality factor (Q). Microwave energy is coupled out of the resonator to a mixer diode through another small hole in the flat plate.

The small waveguide mount acts as a low-Q resonant circuit to excite the diode to oscillation at a frequency determined by its resonant condition. The high-Q resonator is then tuned until its resonant frequency coincides with that of the oscillating diode. The impedance of the high-Q resonator then is dominant for the entire microwave circuit, and the output frequency of the diode locks to its resonance. Any subsequent changes in the resonant frequency of the high-Q structure causes an identical change in the diode's frequency (within its range) by mechanically changing the resonant frequency of the high-Q cavity.

For monitoring purposes, it is necessary to have the resonant frequency of the cavity always tuned exactly to coincide with the known absorption frequency for the molecule of interest. This can be accomplished in a number of ways, one of which is shown in Fig. 2. The frequency of the system is compared with a suitable harmonic of a very stable crystal-controlled oscillator. The analog error signal derived from the comparison is fed back to change the physical dimensions of the cavity and, subsequently, the system frequency. Any short- or long-term frequency variation caused by mechanical instabilities or environmental conditions are compensated by this control loop. The desired frequency can be stabilized to 1 part in 10^8 per day or better in this manner.

Sensitive detection of molecular absorption occurring at the monitored frequency within the cavity can be obtained by using either Stark modulation for electrically polar molecules or Zeeman modulation for magnetically polar (paramagnetic) molecules. The intermediate frequency (IF) carries the modulation information to the IF amplifier where the demodulated IF appears at the video output. This signal is then synchronously detected with the reference from the Stark or Zeeman modulator, resulting in a dc output proportional to the gas absorption in the cavity.

V. Sensitivity for pollutants

It can be shown [2] that the minimum detectable absorption coefficient in cm^{-1} for a resonant-cavity spectrometer is given by

$$\Gamma_{min} = (4kTN \Delta f/P_o)^{1/2} \ (2 \pi/Q_L \lambda), \tag{1}$$

where k is the Boltzmann's constant, T is the absolute temperature, N is the noise figure for the system, Δf is the frequency bandwidth of the detector, P_o is the power incident on the cavity coupling port, Q_L is the loaded Q of the cavity, and λ is the wavelength of radiation.

Many of the common pollutants (e.g., H_2CO, NH_3, SO_2, NO_2) have strong or moderately strong absorption lines in the accessible regions of the microwave spectrum. Formaldehyde, for example, has an absorption line at 28 974.8 MHz [6] with an absorption coefficient of approximately 6×10^{-5} cm^{-1}. The minimum detectable Γ can be calculated using the following values applicable to this H_2CO line. Let $N = 500$, $\Delta f = 0.1$ Hz, $P_o = 10^{-4}$ w, $Q_L = 3 \times 10^4$, and $\lambda = 1.03$ cm. Then $\Gamma_{min} = 1.85 \times 10^{-11}$. Thus, H_2CO in fractional abundance of

approximately $1.85 \times 10^{-11}/6 \times 10^{-5} \approx 0.3$ ppm could be determined in a mixture. This figure is determined for direct monitoring of a gas mixture without preconcentration of H_2CO. With a scheme capable of concentrating H_2CO by a factor of 100, the detection limit for H_2CO in air can be extended to about 3 ppb.

The theoretical minimum detectable limits for other pollutants based on their strongest absorption lines in the 18-GHz to 40-GHz frequency range are $NH_3 \approx 0.02$ ppm, $SO_2 \approx 0.55$ ppm, $NO_2 \approx 3.3$ ppm.

VI. Atmospheric sampling

Most applications for the microwave cavity detector involving pollutant monitoring of the lower atmosphere would require an effective interface with the air. Such an interface should provide a reduction from atmospheric pressure to at least 1 Torr. This transition must take place with a minimum loss in the total number of the molecules of interest, and preferably with an increase in their relative concentration. Gas-permeable membranes can be applied directly for this type of interface.

Separators of gas-permeable membrane have had extensive use in recent years, particularly when both gas chromatography and mass spectroscopy are used. Membranes of various types have different permeation rates for different gases. By maintaining the proper pressure differential across the membrane, enrichments of the more permeable species can be obtained on the low-pressure side. One can choose membrane materials optimized for specific gases. However, in our case a membrane capable of concentrating a number of gases of interest was desirable. Dimethyl-silicone membranes permeate most organic and some inorganic gases much faster than the major constituents of the air, making them very useful for interfacing to the atmosphere. The silicone membranes are commercially available and they were chosen for our work.

The separator used in our work with the pollutants H_2CO, NH_3, SO_2, and NO_2 is shown schematically in Fig. 3. It is machined from stainless steel and is gold plated. It consists of two membrane stages; the first stage has a membrane surface area of 5 cm^2 and the second stage has a surface area of 2.5 cm^2. Each membrane is backed by a 40-mesh screen. O-rings are used between stages for vacuum seals. Provisions are made to pump out between the membranes and to adjust gas flow for optimum relative concentrations of the desired species. The optimum pressure in the space between the two membranes for all gases so far has been found both experimentally and theoretically to be within 4 and 10 Torr when the microwave cell pressure is held between 10 and 100 mTorr. This separator is operated with the microwave spectrometer by mechanically pumping the gases coming through the membrane directly through the cavity absorption cell. The operating pressure within the cell is controlled by adjusting the pumping rate.

VII. Experimental results

Our prototype laboratory model has been used with and without a membrane separator device to determine minimum detectability for two common pollutants, NO_2 and SO_2.

Mixtures of pure helium with calculated concentrations of either NO_2 or SO_2 were prepared with the apparatus shown in Fig. 4. For determination of minimum detectability without the membrane separator, a portion of the mixture was pumped through a needle control valve directly into the cavity absorption cell. The operating pressure within the cell was adjusted to 100 mTorr. The peak response of the spectrometer was recorded for each of the mixtures. A plot of the peak spectrometer signal (in microvolts from the lock-in detector) versus the calculated concentration of trace gas (in ppm by volume) for both NO_2 and SO_2 is shown on the right side in Fig. 5. The measurements were reproducible to within 5%, and the plot shows the average of four separate experiments. The other two plots in Fig. 5 are again for NO_2 and SO_2, but with a dual-stage membrane separator preceding the microwave spectrometer.

Approximately 8 g peak-to-peak of magnetic field (Zeeman) modulation was used with phase-sensitive (lock-in) detection for the NO_2 gas, while 1500 V peak-to-peak of electric field (Stark) modulation was used for SO_2. For this work the minimum detectable concentration for each species was determined as that concentration for which a signal-to-noise ratio of 2:1 was obtained. Without the separator, 11 ppm NO_2 in helium and 3 ppm

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SO_2 in helium were the minimum detectable. With the separator, 55 ppb of NO_2 in helium was minimum. The smallest concentration of SO_2 in helium we could produce (24 ppb) gave a signal-to-noise ratio of 15:1 using the membrane separator. From this work the enrichment factor with membrane separator is found to be about 200 for NO_2 and 750 for SO_2.

The system has also been used to detect pollutants in air mixtures. Figure 6 shows the spectrometer's response to prepared mixtures of 200 and 20 ppm NO_2 in air being carried through the system by helium. Note that helium has no microwave absorption at all because it is strictly non-polar.

Under joint contract to NASA (NASA-L-75902) and the Environmental Protection Agency (EPA-IAG-D179(D)), we have developed a continuous ambient monitor for formaldehyde gas. The instrument consists of a Gunn-diode microwave cavity spectrometer with a two-stage membrane separator preceding it (see Fig. 7). It is simple to operate, easy to calibrate, has long-term stability, is fast responding, and is capable of continuously monitoring formaldehyde in air at levels as low as 10 ppb without interference. This instrument is the practical realization of the use of the physical technique of microwave rotational spectroscopy for pollutant monitoring. We are presently developing an instrument of the same type for ambient monitoring of NH_3 for the State of California Air Resources Board (ARB2-781).

VIII. Conclusions

An attempt has been made in this paper to present substantial evidence that microwave rotational spectroscopy can be developed for use in air-pollution monitoring. Our work with the diode-cavity spectrometer has shown it to be capable of detecting small concentrations of NO_2, SO_2, H_2CO, and NH_3 gas with very high specificity. We feel that with appropriate sample-handling techniques, systems of this type can be developed for multiple-constituent monitoring with a single device. Such an instrument should have broad applicability in today's environmental studies.

Acknowledgments

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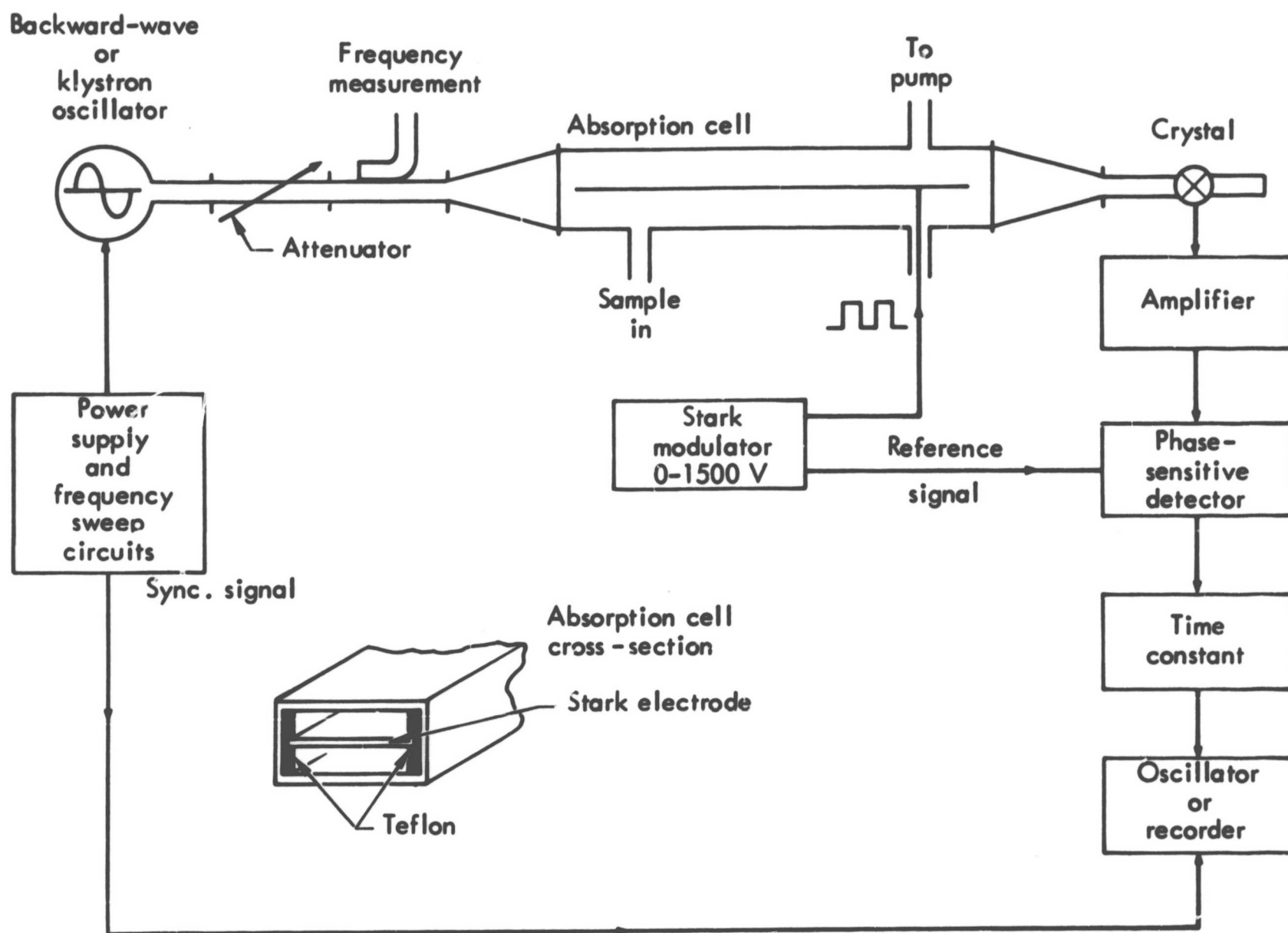
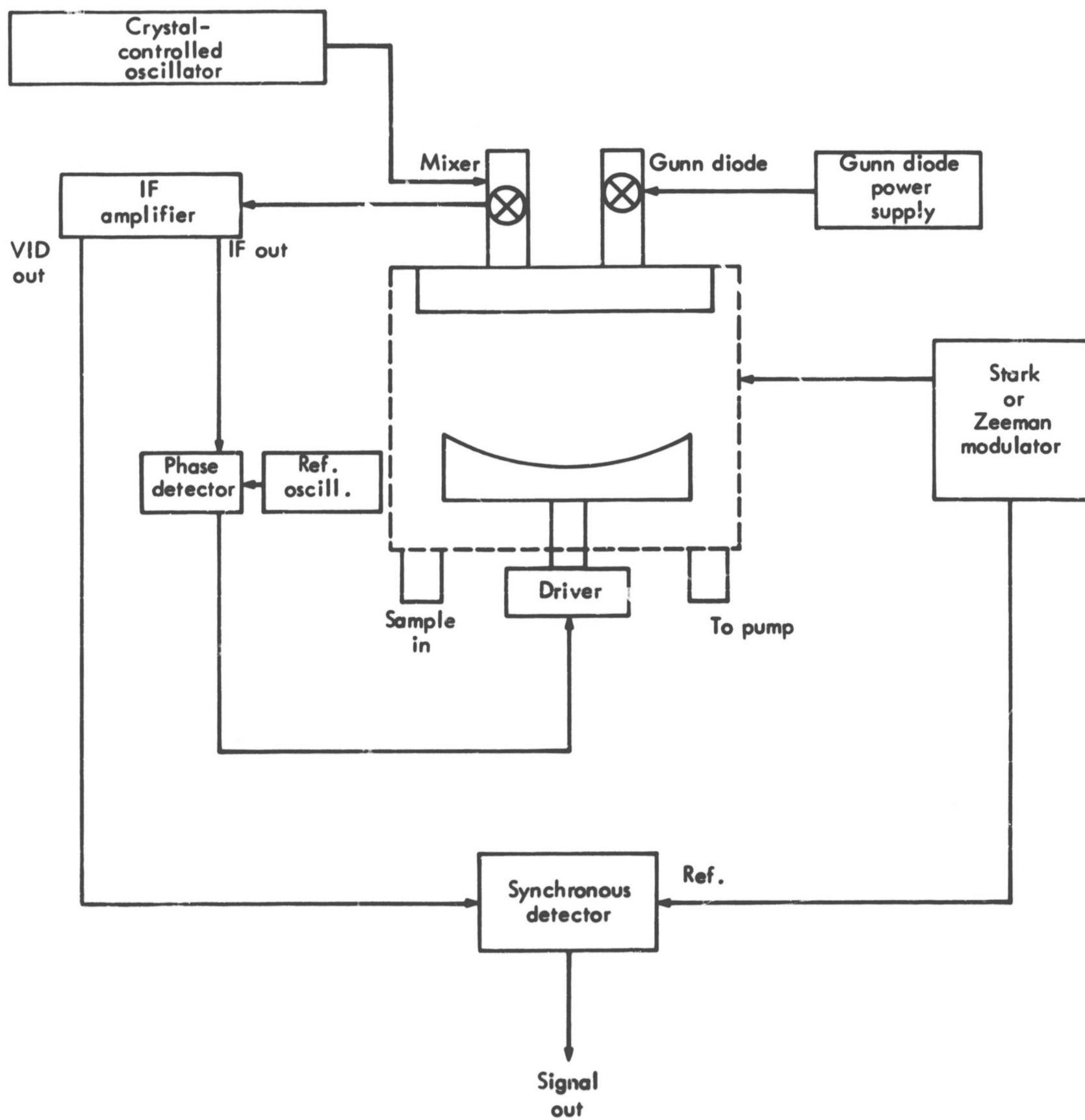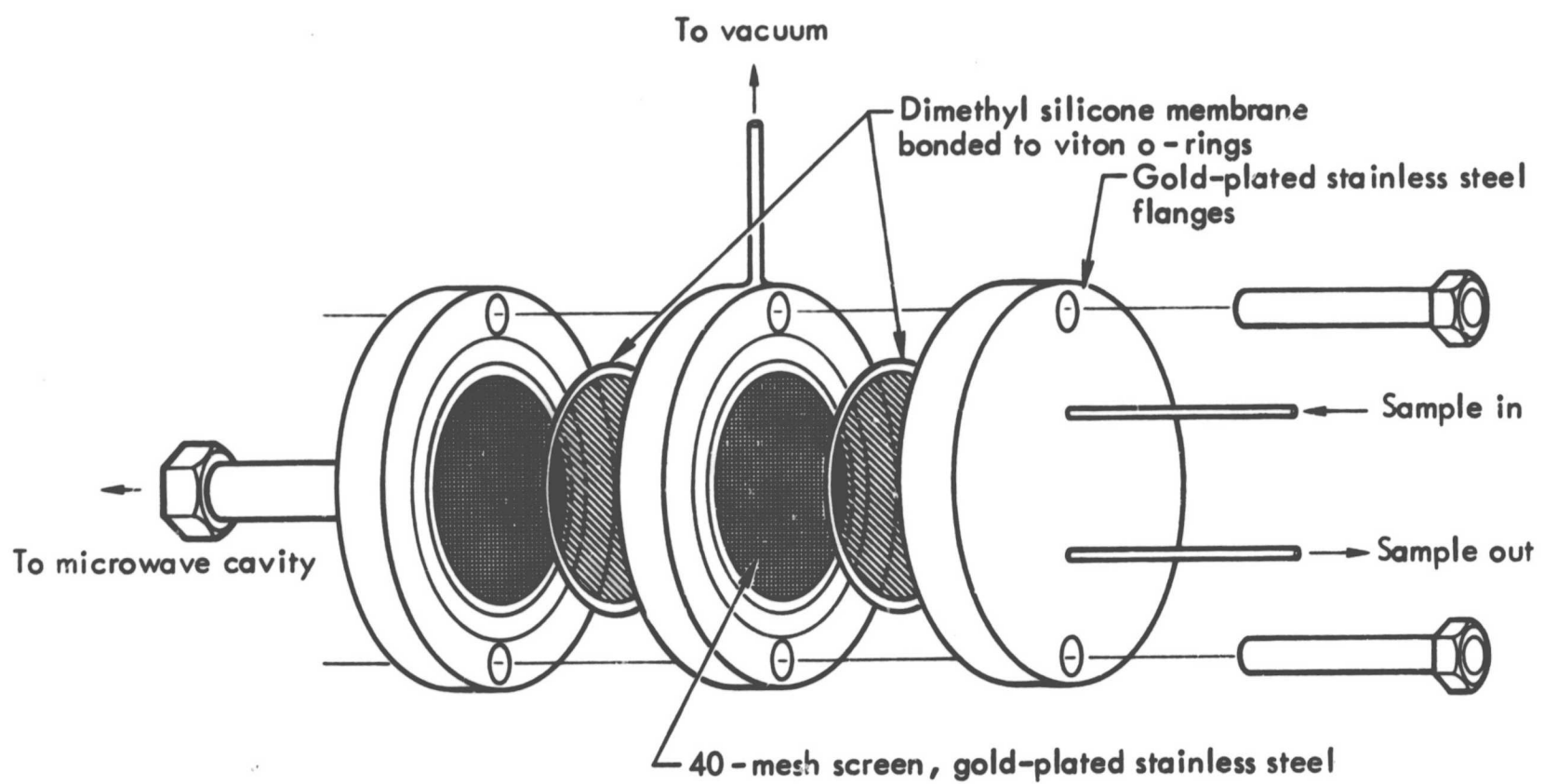Fig. 1. Block diagram of a conventional microwave spectrometer.

Fig. 2. Block diagram of a Gunn-diode microwave cavity spectrometer.

To vacuum

Dimethyl silicone membrane
bonded to viton o - rings

Gold-plated stainless steel
flanges

Sample in

To microwave cavity

Sample out

40 - mesh screen, gold-plated stainless steel

Fig. 3.   Gas-permeable membrane separator.
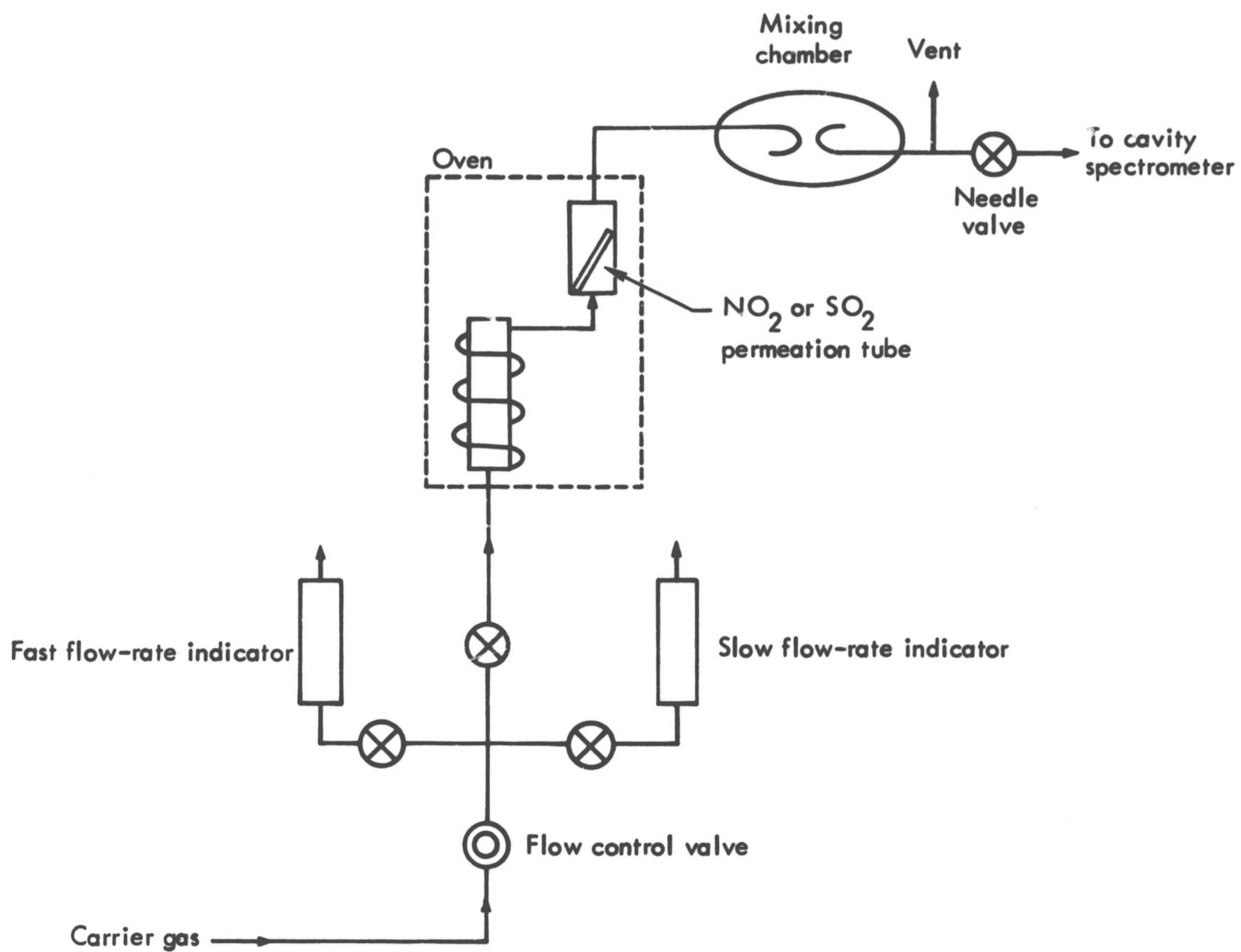
Fig. 4. Schematic of gas-calibration system.
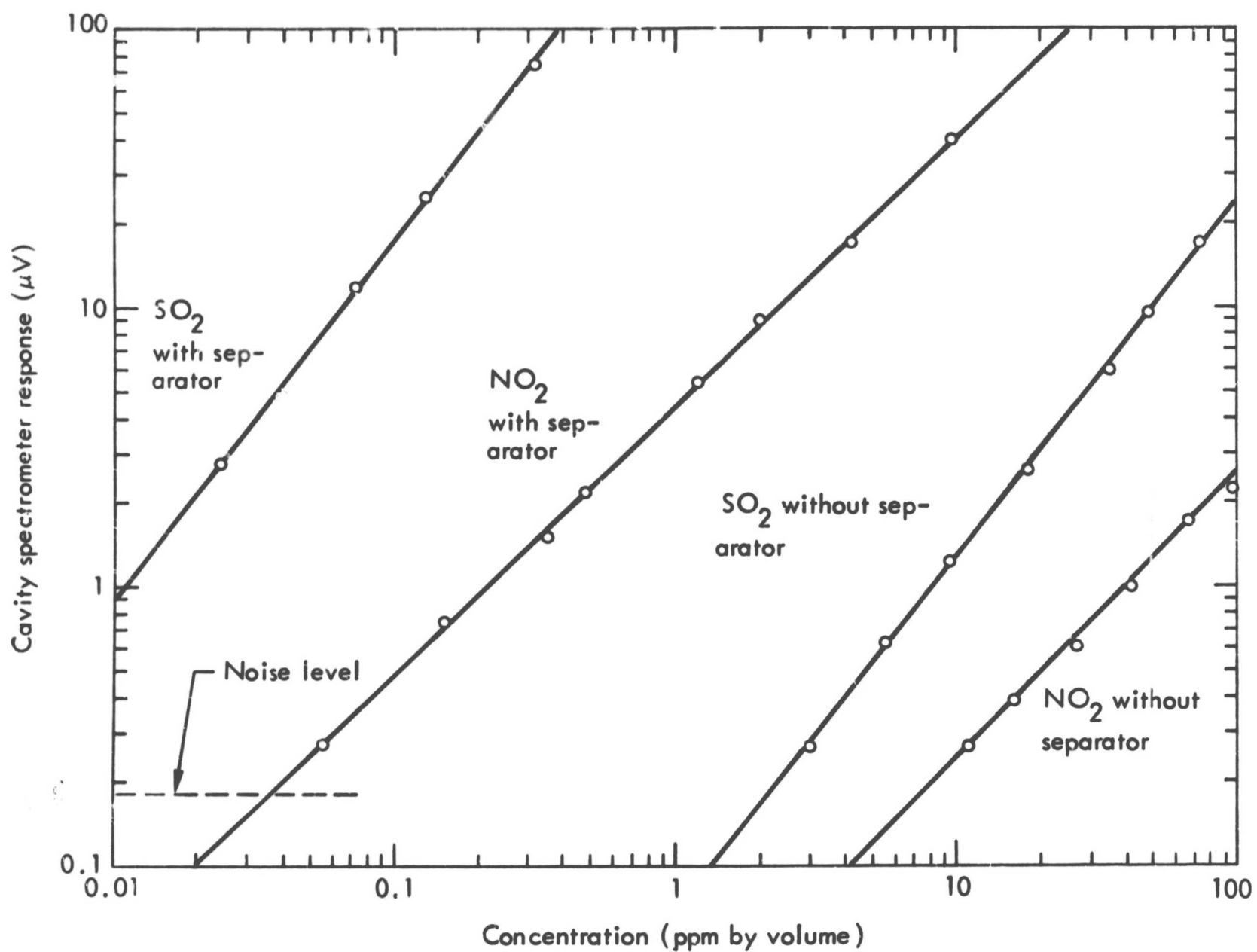
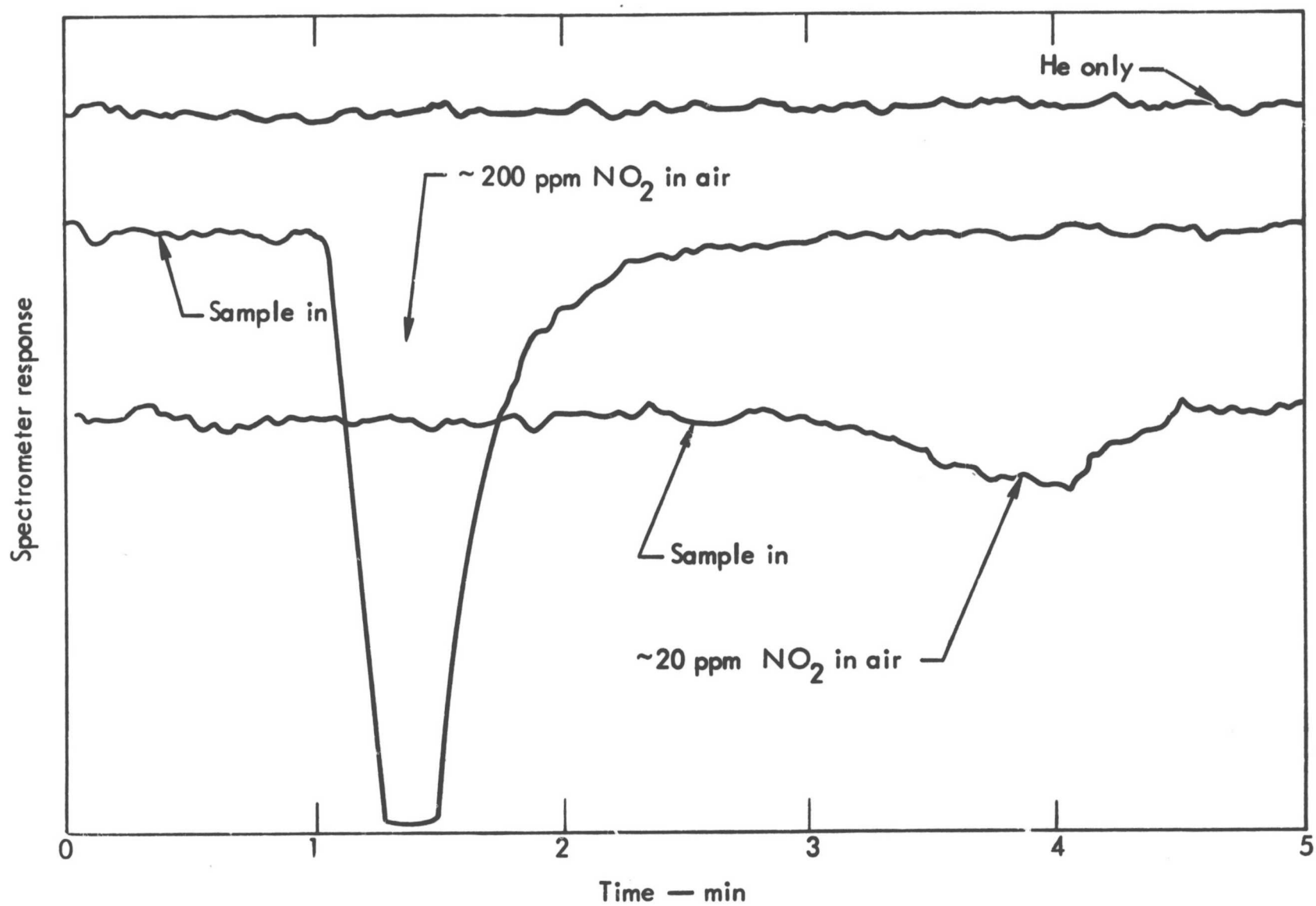Fig. 5. Spectrometer response versus trace concentrations of SO_2 and NO_2.
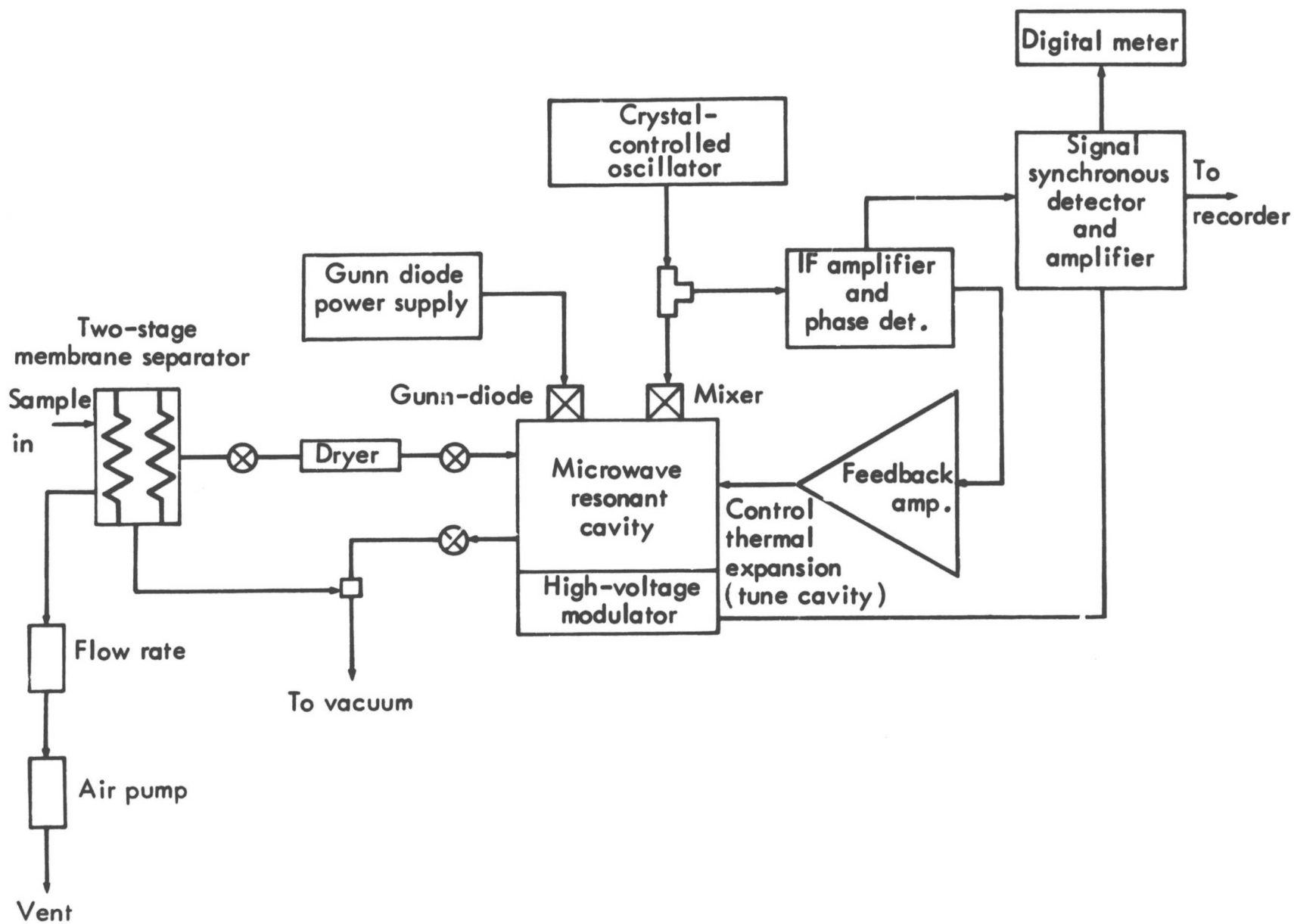
Fig. 6. Detection of NO$_2$ in air with helium carrier.

Fig. 7. Microwave cavity formaldehyde monitor.